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Statement (if applicable):
MW carried out the lab work, data analysis for tribological experiments and wrote the manuscript, BW aided in the lab work and data analysis, JL carried out the analysis of chemical tests, TS and RL secured funding, coordinated the study and critically apraised the manuscript.

The composition and friction reducing properties of leaf layers

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May 26, 2020

Abstract

Every autumn rail networks across the world suffer delays, accidents and schedule changes due to low friction problems caused by leaves landing on the rails. These leaves form a layer that can reduce the friction between the wheel and the rail to a similar level as that between ice and an ice-skate ($\mu = 0.01 - 0.05$). Previous works have generated several hypotheses for the chemical reactions and low friction mechanism associated with these layers.

In this work, the reaction between an aqueous extract of sycamore leaves and metallic iron is investigated. This reaction has been shown to produce a black precipitate, which matches field observations of leaf layers, while friction tests with these extracts produce characteristic ultra low friction. The reaction is investigated through FTIR, XPS, CHNS and ICP-MS analysis as well as wet chemical testing. The impact of the reaction on friction is investigated through three rounds of tribological testing.

The results indicate that the black precipitate produced is iron tannate, formed by complexation of tannins with dissolved iron ions. Friction testing showed that eliminating tannins from the leaf extract resulted in a significant increase in friction coefficient compared to the control.

1 Introduction

In the United Kingdom, transport is responsible for 40% of total energy consumption, using 57 million tonnes of oil equivalent per year [1]. Rail travel offers the most carbon efficient mode of passenger transport available, with local rail services even out preforming electric cars charged from the grid [2]. However, rail travel only accounts for 10% of the total passenger kilometres travelled [3]. Dissatisfaction in rail services is driven primarily by delays [4], with seasonal delays caused by leaf fall being notoriously problematic [5]. Field observations and laboratory tests indicate that fallen leaves leaves are crushed in the wheel-rail contact leaving a black layer [6, 7]. In wet conditions this black layer can reduce the maximum friction coefficient between the wheel and the rail to 0.01

[8]. However, the actual low friction mechanism and contributing parts of the composition are not known.

Many forms of tribological testing with leaves trapped in the contact have been described in the literature. Rolling-sliding tests typically give friction coefficients of 0.01-0.05 [9, 10] in line with field trials [6, 7], while pure sliding, pin-on-disc type tests give friction coefficients in the 0.1-0.3 range [11, 12, 13]. Variability in results with leaves as the lubricant has led some researchers to test with aqueous leaf extracts. Rolling sliding tests with these extracts have given friction coefficients as low as 0.03 while also producing a black layer on the test specimens [14, 13, 15]. Cann concluded that this was the result of dissolved pectin increasing the viscosity of the extract [14], but subsequent tests have shown that the viscosity of leaf extracts is not significantly different from water [13].

A diverse set of chemical tests have been carried out on leaf layers [10, 16, 13] with the aim of developing chemical mitigation methods, however much of this work suffers from similar problems. The wheel-rail contact is highly contaminated and leaf chemistry is complicated, these two factors mean that a wide variety of chemicals can be found in the layer, however, the presence of a chemical does not imply that it is important to the low friction phenomenon. These tests have generated many hypotheses for the chemical reactions which occur, however, no studies have set out to test these hypotheses or demonstrate the relevance of a particular chemical reaction to friction.

This problem has remained inscrutable to both chemical analysis and experimental tribological testing. In this work we present the results of a multidisciplinary approach. This consisted of selecting a hypothesis from the literature, designing chemical extractions and testing the effects on friction with tribological testing. For brevity, we present only evidence relating to the hypothesis that was accepted, that the black layer is iron tannate produced by a reaction between tannins and dissolved iron.

2 Results

2.1 Reactions with dissolved Iron

Previous analyses [14, 13] have reacted leaf extract solutions with steel plates, the function of the steel plate is not known, however it is likely that iron ions dissolved by the acidic leaf extract react to cause the black precipitate. To investigate this, samples of brown leaf extract solution (BLE) were prepared and reacted with iron (III) chloride solutions. $0.01M/l$ solutions of $FeCl_3$ were added to $10ml$ leaf extracts as shown in Table 1. This resulted in a fast reaction producing a black precipitate in the liquid. The precipitate was filtered out and the iron content of the resulting filtrate was investigated by inductively coupled plasma mass spectrometry (ICP-MS). The results of this analysis (Table 1) indicate that some of the iron is removed from the solution in the black precipitate.

Sample number	vol. H_2O (ml)	vol. BLE (ml)	vol. $FeCl_3$ $0.01M/l$ (ml)	IC Fe mg/l
1	0	10	0	0.00
2	0	10	0.5	3.058
3	0	10	0.1	1.314
4	10	0	0.5	8.192

Table 1: Details of experiments and results from ion chromatography

This was confirmed through XRF of the washed filter cakes. This showed iron was present in the filter cake, no other elements within the detection limit of the instrument (elements heavier than Si) could be detected. Full spectra, labelled with common elements are available in the additional material. These results show that the iron is not only acting as a catalyst.

2.2 Effect of removal of poly-phenols

Poly-phenols, including tannins, can be partially extracted from solutions using Polyvinylpolypyrrolidone (PVPP) as described in the materials and methods. The effect of this treatment on both the immediate change in colour and the mass of the filtered precipitate was investigated.

The colour change observed on the addition of aqueous $FeCl_3$ to BLE was quantified though visible light spectrometry. Samples of brown leaf extract (BLE), PVPP treated BLE and the elute from the first PVPP treatment were prepared as described in the materials and methods. Visible light spectra were obtained for each sample to act as a baseline. $3ml$ of each sample was then mixed with $50\mu l$ of $FeCl_3$ solution ($0.01M/l$). A second spectra was obtained immediately after mixing and the mean difference between the two spectra was taken as a measure of the colour change.

The entire experiment including extraction was repeated in triplicate and the results analysed by a one way ANOVA with Bonferroni's post tests. The results of the experiment are presented in Figure 1A, these show that the PVPP treatment almost entirely prevents the colour change on addition of $FeCl_3$ solution ($p < 0.00001$), while the tannins eluted from the PVPP by aqueous acetone show a significant colour change compared to water ($p < 0.00001$).

Additionally the yield of solid product from the reaction was investigated. $10ml$ samples of BLE and PVPP treated BLE were mixed with $500\mu l$ of $FeCl_3$ solution ($0.01M/l$) and heated for 2 minutes at 80°C. The mixture was then filtered and the filter cake was dried in a vacuum oven at $50°C$ for 30 minutes. The mass of the dried filter cake was recorded. The experiment was repeated in triplicate. The results are shown in Figure 1. Extraction of poly-phenols by PVPP treatment reduced the weight of the filter cake by an average of 82% ($p = 0.00038$).

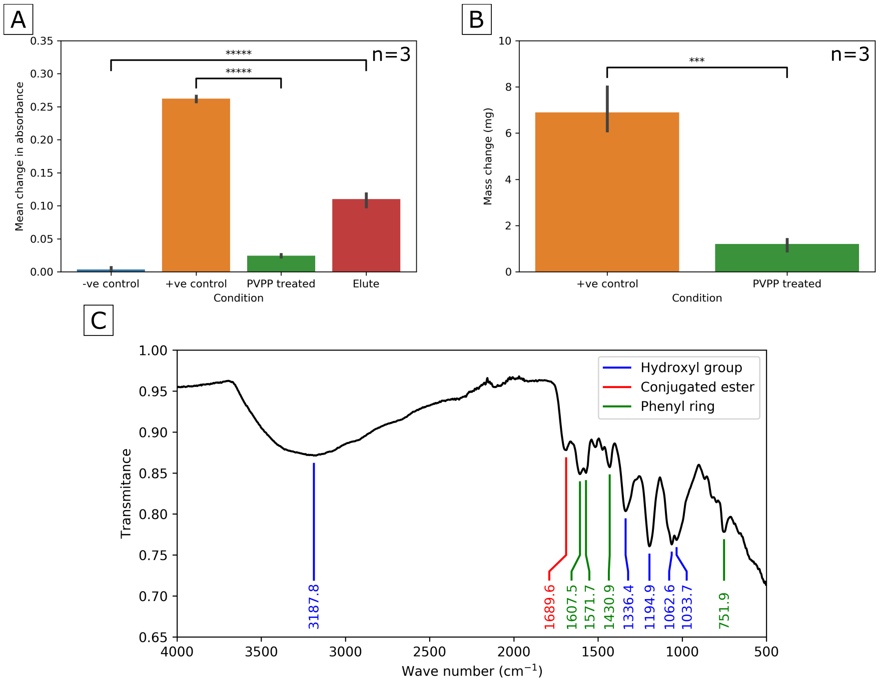

Figure 1: Results from chemical tests. (A) The results of the visible light spectroscopy, (B) the weight of the filter cakes from raw BLE (control) and PVPP treated BLE ($n = 3$, $p = 0.00038$, one sided t-test, unequal variance), (C) and the FTIR spectra of the dried precipitate

Element	CHNS composition $\%wt$ $(n=3)$	XPS composition $\%at$ $(n=3)$	combined atomic
C	39.3	66.4	83
H	4.7	-	119
N	< 0.3	0.3	0.38
S	< 0.3	0.1	0.13
O	-	32.5	41
Fe	-	0.8	1

Table 2: The results from CHNS and XPS analysis of the washed and dried precipitate

2.3 Characterisation of the black precipitate

Black precipitate was generated by mixing filtered BLE with iron chloride as described above. The precipitate was filtered out of the solution, washed with distilled water and dried in a vacuum oven at 50°C for 30 minutes. The result is a solid, black, shiny material, similar in appearance to a plastic. The material has a hardness of $352 \pm 2MPa$ and a modulus of $6.90 \pm 0.29GPa$, measured by instrumented nano indentation (averaged across 9 samples).

The composition of the sample was investigated by both CHNS analysis and XPS with results shown in Table 2. As shown the nitrogen content of is 0.3% by weight, the accuracy of the analyser was 0.3%. By combining the XPS and CHNS results a rough formula for the black precipitate can be established as: $C_{83}O_{41}H_{119}.Fe$. The trace amount of nitrogen present in the sample is attributed to contamination and ignored.

An FTIR spectra of the dried precipitate is shown in Figure 1C, the analysis method given in [17] was used to interpret the spectra. The broad band at $3187cm^{-1}$ is indicative of hydroxyl groups with inter molecular hydrogen bonding [17, 18, 19]. The presence of further moderate to strong bands in the regions 1600-1300 (O-H) and 1200-1000 (C-O) is additional evidence of this [17].

No sharp absorption bands were observed above $3000cm^{-1}$ (the $C-H$ stretching region). However, these are typically not observed for tannic acid or its complexes with iron ions [18, 19], despite the presence of C-H bonding.

Absorption at $1689cm^{-1}$ is typical of a hydroxyl group, and can be explained by a simple carbonyl such as an ester, conjugated by an aromatic ring[17]. Additional complexation with an iron ion also shifts this peak to lower wave numbers [19].

The presence of aromatic rings is supported by the strong peak at $1607cm^{-1}$ and additional peaks at 1571, 1516, & $1473cm^{-1}$ which all lie within the $C=C$ stretch region. Weak peaks in the out of plane C-H bending region $850-670cm^{-1}$ also support the presence of aromatic rings, these peaks are typically weakened by complexation with iron ions [19].

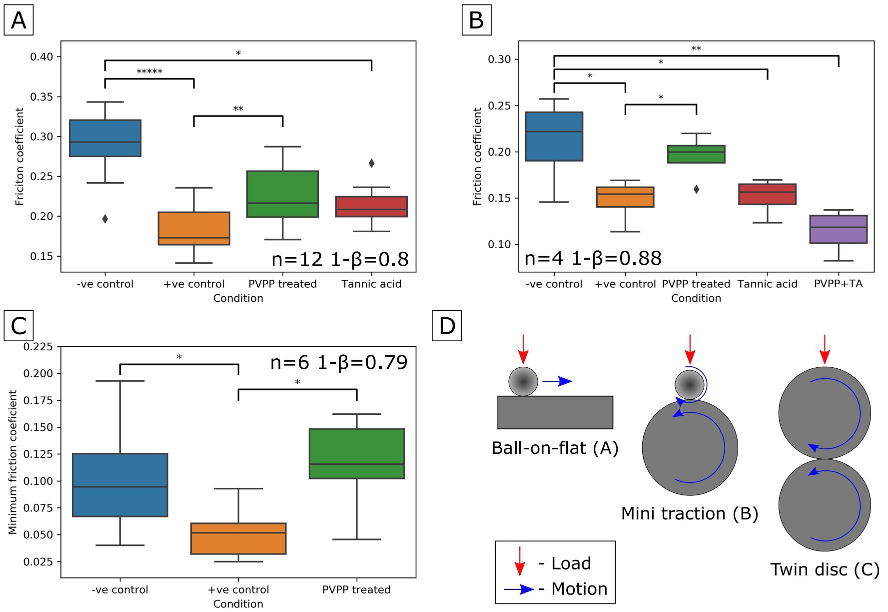

Figure 2: The results of tribological testing of the leaf extracts. (A) ball-on-flat; (B) mini traction; and (C) twin disc tests. (D) Schematic representations of each of the test configurations (D). Significance indicators have the following meanings: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, **** $p < 0.0001$, ***** $p < 0.00001$. p-values are calculated by t-test of the ordinary least squares model parameter after controlling for order and sample effects.

2.4 Tribological tests

The results from the chemical tests presented above are concordant with the hypothesis that the black precipitate is iron tannate, produced by a reaction between poly-phenols and dissolved iron [13]. However, they do not show if this reaction is important in terms of friction available at the interface. As such, three rounds of tribological testing were run to test the hypothesis that tannins in the leaf extract reduce the friction coefficient of the interface.

The results of the ball on flat testing are shown in Figure 2A. Both the untreated leaf extract and tannic acid solutions showed significantly lower friction than the negative control (water). A significant difference was also observed between the PVPP treated leaf extract and the positive control (untreated leaf extract), showing that the removal of tannins increases the friction coefficient in pure sliding. No other statistically significant differences were observed including between the positive control and the iron tannate groups.

The effect of tannins on friction was further investigated by rolling-sliding, ball on ring tests. The results of this experiment are shown in Figure 2B. These experiments included both artificial tannic acid solutions and PVPP treated leaf extract with tannic acid replaced. Again significantly lower friction is observed for all solutions containing tannins when compared to the water negative control. The PVPP treatment is also associated with a significant increase in friction compared to the untreated leaf extract.

More representative, twin disc, rolling-sliding tests were completed on the Sheffield University rolling-sliding rig as described in the methods section. The results of these tests are shown in Figure 2C. These results reproduce the same trends discussed above, with untreated leaf extract which contains tannins giving significantly lower friction than either water or PVPP treated leaf extract ($p = 0.015$ mean, 0.032 minimum) and PVPP treated leaf extract not being significantly different from water ($p = 0.92$ mean, 0.54 minimum). In these results the extremely low friction found in full scale field trials was also recreated.

The full results from each test and the analysis code used to analyse data and produce figures is included in the additional material.

3 Discussion

The chemical results shown above indicate that the black precipitate is caused by a species which is adsorbed by PVPP, and can be eluted with aqueous acetone. FTIR of the precipitate shows evidence of hydrogen bonding caused by hydroxyl groups, aromatic rings and esters. Tannins are poly-phenols which are abundant in a wide variety of plant leaves [20, 19], many of these are soluble in water. This class of molecule fits well with the evidence above and is highly likely to be present in leaf extracts.

Complexation of ionic iron by tannins has been studied intensely due to its use in early inks, corrosion coatings and medicine. It is know to produce a black precipitate with an FTIR spectra which closely matches that found in this study [18, 19]. During this reaction the iron ions are chelated by dissociated hydroxyl ligands on the tannins [21]. At neutral pH this causes cross linking between tannin molecules, while at low pH the reaction is reversed [21].

The tribological results show that tannins reduce friction in both pure sliding and rolling-sliding contacts. While many works have speculated that cellulose in the leaves forms a lubricating layer, these results show that this is not necessary for low friction conditions. They also indicate that the mechanism of friction reduction is by dynamic lubrication, as experiments with lower contact pressures and higher rolling speeds showed the lowest friction.

In the context of the existing literature, these results point to a likely low friction mechanism for leaf contaminated wheel-rail contact. The cross linked tannin molecules form a loosely bonded hydro gel [21], when this is compressed in the contact the water can be squeezed out of the structure. Thus, the reacted leaf extract is initially a strongly piezo-viscous lubricant that will prevent metal to metal contact. Confirming the nature of the low friction mechanism will be the subject of future work.

As the wheel rail contact is an open system, these results cannot show that the mechanism found in the field is exactly and only the mechanism shown here. For example, while these results shown that cellulose is not required for low friction it is still possible that it, or any other contaminant or combination of contaminants may cause low friction. It is not possible, or our intention, to disprove all other potential low friction mechanisms. However, we have presented strong evidence that tannins alone can cause low friction, and other chemicals in the leaf extracts cannot. With this chemical reaction found and linked to low friction phenomena, interventions can be designed to target the specific reactions or chemicals presented above.

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5 Materials and methods

Unless otherwise stated all reagents were purchased from Sigma-Aldrich Ltd. (U.K.). All filtering, unless otherwise stated, was performed with cellulose filter membranes with a pore size of $0.49 \mu m$ (purchased from Agilent technologies).

5.1 Generation of leaf extracts

In this study brown leaf extract (BLE) was prepared and tested using a variety of techniques. The extract was prepared in accordance with the method given in [5], which will be related in brief here. Brown sycamore leaves which had naturally fallen were collected during the autumn of 2018, these were milled into a mulch with an average particle size of $5mm$, and frozen at -8°C for storage.

When a BLE sample was required, the frozen mulch was mixed with distilled water in the proportion 1g to 50ml. This was left for 60 hours at room temperature with no mixing. The resulting suspension was filtered to remove the large debris. This method is in accordance with Ishizaka et al. [5], however for this study all BLE suspensions are further filtered down to $0.49 \mu m$ resulting in a clear brown solution with a pH of 4.8.

Work with this solution has shown it to be unstable at room temperature, with a shelf life of no more than 4 days, attempts to freeze the solution to $-8°C$ increase this to the order of weeks however degradation still occurs, sterilising the solution prior to storage has no effect. To the authors' knowledge, this problem has not been mentioned in the context of rail research until now and it is possible that previous analyses have been carried out on degraded samples. In order to mitigate this problem, all chemical analysis, reactions and tribological tests presented in this work are completed with fresh leaf extracts on the day of preparation.

5.2 PVPP treatment of leaf extracts

Polyvinylpolypyrrolidone (PVPP) has been shown to bond with tannins in organic solutions causing them to be removed from the solution [22, 23]. In this work PVPP has been used as a convenient method for removing tannins from the leaf extract solutions.

This extraction is performed by mixing PVPP powder ($100\mu m$ particle size) and filtered leaf extract in the ratio 1g to 10ml. The mixture is stirred continuously for ten minutes at room temperature and filtered to remove the PVPP. This extraction is repeated 3 times. Where species are eluted from the PVPP only the first batch is used.

For some tests tannic acid powder was added to PVPP treated solutions. This was done Colorimetrically with tannic acid powder being added until the absorbance of the solution in the $600 - 1000nm$ was within 5% of the value for raw leaf extract from the same extraction. This could be adjusted in either direction by the addition of tannic acid powder or PVPP treated extract. This procedure was also followed for pure tannic acid solutions.

5.3 Chemical tests

Dissolved iron was quantified by ICP-MS, samples were diluted (x10) and acidified to $1\%v/v\ HNO_3$ before analysis. Certified standards were used. Samples were run in duplicate and at two different masses to account for interference.

XPS analyses were carried out using a Kratos Supra instrument with a monochromated aluminium source, and two analysis points per sample. The analysis area was 700 by 300 μm. Charge neutralisation was used throughout. The survey scans were collected between 1200-0 eV, at 1 eV energy resolution, and two 300 second sweeps. High resolution O 1s, C 1s, N 1s, Na 1s, Ca 2p, Cl 2p and S 2p scans were collected over an appropriate energy range at 0.1 eV energy resolution, and 300 seconds per sweep. Two sweeps were collected for N 1s and S 2p, and three for C 1s since the energy range had been extended to include the K 2p peaks, one sweep was considered enough for all other high resolution scans.

The data collected was calibrated in intensity using a transmission function characteristic of the instrument to make the values instrument independent. The data are then quantified using theoretical Schofield relative sensitivity factors. All data has been calibrated relative to a C 1s position of 285.0 eV for C-C/C-H type carbon environments.

X-ray florescence measurements were performed on an Fischerscope X-RAY XAN 250 (Fischer Technology, Inc., Windsor, CT, USA). A $2mm$ diameter area of each sample is examined. A potential of $50kV$ was used with a primary Nickel filter, the measurement time was 60 seconds per sample.

Fourier transformed infra-red spectroscopy (FTIR) was performed on a Bruker Alpha with a Diamond ATR accessory (single bounce). The average of 64 scans was taken to improve resolution and a background measurement was taken and subtracted from the measurement (also 64 scans). Scans were completed at

23°C.

CNHS analysis was performed on a Vario MICRO cube analyser with a detection limit of 0.3% and an accuracy of 0.3%, samples were run in triplicate.

Visible light spectrometry was performed on a Varian Cary 50 in the range 400 to 1000nm. Controls were run before the analysis to ensure the measured values were with in the measurement range, samples are only compared to controls with the same dilution factors.

5.4 Tribological tests

In this study, three different testing methods are used to investigate the effect of leaf components on the friction available at the interface. Ball on flat testing is used to investigate pure sliding behaviour while rolling-sliding contact is investigated through tests on a mini traction machine and the Sheffield University rolling-sliding rig. All tests were run at room temperature.

Ball on flat tests were preformed on a Bruker UMT3, each tribological test used identical specimens, flat specimens were made from EN24T sheet with a ground surface finish (RA=1μm), balls were 5mm diameter AISI 316 stainless steel. Tests were completed at a normal load of 10N leading to an initial maximum contact pressure of 1.55 GPa. Reciprocating tests were used as they allow for multiple, tests from the same flat specimen. A stroke length of 10mm was used with a speed of 4 mm/s.

After a dry running in period of 50 strokes, the mean friction force result from the first 50 full strokes was taken, the data are not filtered before averaging. Outliers were removed if their absolute z score was greater than 2.5 (more than 2.5 standard deviations from the mean of the sample). Five tests were performed per flat sample, between each test the ball was replaced and the flat sample cleaned with isopropanol (cleaning grade) to remove the test solution.

Tests and samples were randomised, the test operator was blinded to the lubricant which was to be applied during cleaning, set up and running in. After the samples had been run in, the lubricant to be used was revealed to the tester, the tester then applied 200μl of the lubricant and ran the test. This was done to minimise the possibility of introducing bias during set up or cleaning of the samples. No tests were stopped after the lubricant had been revealed. 200μl was sufficient to flood the contact area.

The test conditions are summarised in Table 3. Before testing, the statistical power of the study was assessed and this was used to decide the number of repeats needed. Assuming that the smallest effect of interest is a 30% change in mean friction force and that the coefficient of variation of results will be 25% [**?**], a statistical power of 0.78 at the $p = 0.05$ significance level is achieved by repeating tests 12 times ($n = 12$). This means that, the chance of missing a real change in mean friction force of 30% is 0.22, while the chance of a false positive result is 5% (p).For larger changes the chance of missing a real change is reduced. Sample sizes were kept equal between all groups, thus the F statistic is robust to deviations from normality and inhomogeneous variance.

	Parameter	Ball on flat	Mini traction	Twin disc
Body 1	Radius (mm)	2.5	12.7	23.5
	Roughness ($R_a,\ \mu m$)	≤ 0.1	≤ 0.1	1
	Surface speed (mm/s)	0-4	60	970
Body 2	Radius (mm)	Flat	23.5	23.5
	Roughness ($R_a,\ \mu m$)	1	1	1
	Surface speed (mm/s)	0	100	1000
Contact	Load (N)	10	44	2720
	Hertzian pressure (GPa)	1.55	1	0.9
	Hertzian half width (mm)	0.0555 0.0555	0.126 0.167	0.19 -
	Sliding speed ($U_r,\ mm/s$)	0-4	40	30
	Rolling speed ($U_r,\ mm/s$)	0-2	80	985
	Sliding to rolling ratio (%)	200	50	3
	Lubricant volume (μl)	200	200	300
Experiment	Repeats per condition (n)	12	4	6
	Threshold p-value	0.05	0.05	0.05
	Estimated power	0.78	0.88	0.81
Lubricants	PVPP treated	X	X	X
	Tannic acid	X	X	
	PVPP + tannic acid		X	

Table 3: Test conditions for all tribological tests completed in this work. All experiments included a positive and negative control group, these were untreated leaf extract and water respectively

Mini traction tests were performed on a Phoenix Tribology TE 54 mini traction machine, with a ball and roller set up. During these tests a $25.4mm$ diameter is loaded against a $47mm$ diameter ring. The speed of the ring was $0.1m/s$ and a sliding to rolling ratio of 50% was used. Samples were cleaned in pentane immediately prior to testing.

The tests consisted of a dry running in phase lasting $100s$ after which $200\mu l$ of lubricant was applied and the test continued for another $100s$. Again $200\mu l$ was sufficient to flood the contact patch. The mean friction coefficient during the second $100s$ was taken as the response variable. Using data from [14] the likely standard deviation in the results was estimated as 2% of the wet value. This was used to design an experiment as shown in Table 3. As above tests and samples were randomised and the operator was blinded to the lubricant until test had begun.

Twin disc tests were performed on the University of Sheffield rolling-sliding test rig (SUROS). The SUROS rig applies a normal force to two counter-rotating steel discs, one manufactured from wheel and one from rail material. The $47mm$ diameter discs, one driven by a Colchester Mascot lathe and the other by an AC motor, rotate at different speeds which produces slip in the contact. A more detailed description of the SUROS rig is given Fletcher and Lewis [**?**].

The discs were ultrasonically cleaned in acetone to remove any contaminants and then left to dry before mounting. The rail specimen was mountain to the lathe (upper) and the wheel specimen was mounted to the AC motor (lower). The rail specimen was run at $400rpm$, with the wheel specimen rotated faster to produce the desired sliding to rolling ratio (SRR). A SRR of 3% was applied as this is the minimum value at which the entire contact is sliding. A normal load was applied to give a maximum Hertzian contact pressure of $900MPa$, which simulates the conditions of a typical UK passenger locomotive, with a $75kN$ axle load.

Discs were run in under dry conditions until the traction coefficient reached 0.4. A this point $300\mu l$ of lubricant was added, causing a drop in the traction coefficient. The test continued to run with no additional lubricant until the traction coefficient reached 0.4 again. This process was repeated six times on each pair of samples. While this methodology allows cross contamination between the lubricants it also allows more repeat tests without confounding disc material and lubricant effects. In preliminary testing 500 cycles were allowed between lubricants however the wear during dry running resulted in unrealistic rough disc surfaces.

The rolling-sliding tribological experiment was designed with the parameters shown in Table 3, requiring 6 repeats to give a statistical power of 0.86 at the 0.05 significance level, the likely variation in the results was estimated from Cann et al. [14]. Due to the chance of cross contamination during testing, each permutation of the order of application was included. The order of these permutations was randomised and the experimenters were blinded to the lubricant to be applied until the moment of application.

The data from each of the tests were analysed by an ordinary least squares model. The lubricant factors of the model were tested by t-tests after controlling for order and sample effects. The Python 3.6 codes used to design these experiments, randomise the test conditions, blind the operators and analyse the data is included in the additional material. In order to run, the package statsmodels (version 0.9.0) must be installed. In addition, the seaborn (version 0.9.0) and jupyter (version 1.0.0) packages are required to run the data analysis code.

References

[1] National Statistics. Energy Consumption in the UK (ECUK) 1970 to 2018. Technical Report July 2019, 2019.

[2] Nikolas Hill, Helen Walker, Jamie Beevor, and Keith James. 2011 Guidelines to Defra / DECC's GHG Conversion Factors for Company Reporting: Methodology Paper for Emission Factors Contents. Technical Report August, 2011.

[3] Department for Transport. Transport Statistics Great Britain 2018. pages 1–30, 2018.

[4] TransportFocus. National Rail Passenger SurveyMain Report Spring 2019. Technical report, 2019.

[5] Kei Ishizaka, Stephen R. Lewis, and Roger Lewis. The low adhesion problem due to leaf contamination in the wheel/rail contact: Bonding and low adhesion mechanisms. *Wear*, 378-379:183–197, 2017.

[6] K Nagase. A study of adhesion between the rails and running wheels on main lines : results of investigations by slipping adhesion test bogie. 203, 1989.

[7] O. Arias-Cuevas, Z. Li, R. Lewis, and E. A. Gallardo-Hernández. Laboratory investigation of some sanding parameters to improve the adhesion in leaf-contaminated wheel—rail contacts. 224(3):139–157, 2010.

[8] Z. Li, O. Arias-Cuevas, R. Lewis, and E. A. Gallardo-Hernández. Rolling-sliding laboratory tests of friction modifiers in leaf contaminated wheel-rail contacts. *Tribology Letters*, 33(2):97–109, 2009.

[9] E. A. Gallardo-Hernandez and R. Lewis. Twin disc assessment of wheel/rail adhesion. *Wear*, 265(9-10):1309–1316, 2008.

[10] S. R. Lewis, R. Lewis, J. Cotter, X. Lu, and D. T. Eadie. A new method for the assessment of traction enhancers and the generation of organic layers in a twin-disc machine. *Wear*, 366-367:258–267, 2016.

[11] U. Olofsson and K. Sundvall. Influence of leaf, humidity and applied lubrication on friction in the wheel-rail contact: Pin-on-disc experiments. *Proceedings of the Institution of Mechanical Engineers, Part F: Journal of Rail and Rapid Transit*, 218(3):235–242, 2004.

[12] Y. Zhu, Y. Lyu, and U. Olofsson. Mapping the friction between railway wheels and rails focusing on environmental conditions. *Wear*, 324-325:122–128, 2015.

[13] Kei Ishizaka, Stephen R. Lewis, Deborah Hammond, and Roger Lewis. Chemistry of black leaf films synthesised using rail steels and their influence on the low friction mechanism. *RSC Advances*, 8(57):32506–32521, 2018.

[14] P. M. Cann. The ”leaves on the line” problem - A study of leaf residue film formation and lubricity under laboratory test conditions. *Tribology Letters*, 24(2):151–158, 2006.

[15] Milan Omasta, Martin Machatka, David Smejkal, Martin Hartl, and Ivan Křupka. Influence of sanding parameters on adhesion recovery in contaminated wheel-rail contact. *Wear*, 322-323:218–225, 2015.

[16] Yi Zhu, Ulf Olofsson, and Rickard Nilsson. A field test study of leaf contamination on railhead surfaces. *Proceedings of the Institution of Mechanical Engineers, Part F: Journal of Rail and Rapid Transit*, 228(1):71–84, 2014.

[17] John Coates. Encyclopedia of Analytical Chemistry -IInterpretation of Infrared Spectra, A Practical Approach. pages 1–23, 2004.

[18] J. Iglesias, E. García de Saldaña, and J. A. Jaén. On the Tannic Acid Interaction with Metallic Iron. *Hyperfine Interactions*, 134(1):109–114, 2001.

[19] Y. M. Li, X. Miao, Z. G. Wei, J. Cui, S. Y. Li, R. M. Han, Y. Zhang, and W. Wei. Iron-tannic acid nanocomplexes: Facile synthesis and application for removal of methylene blue from aqueous solution. *Digest Journal of Nanomaterials and Biostructures*, 11(4):1045–1061, 2016.

[20] Olivier André, Pierre Vollenweider, and Madeleine S Günthardt-Goerg. Foliage response to heavy metal contamination in Sycamore Maple (Acer pseudoplatanus L.). *For. Snow Landsc. Res*, 80(3):275–288, 2006.

[21] Lin Fan, Yanyan Ma, Yanlei Su, Runnan Zhang, Yanan Liu, Qi Zhang, and Zhongyi Jiang. Green coating by coordination of tannic acid and iron ions for antioxidant nanofiltration membranes. *RSC Advances*, 5(130):107777–107784, 2015.

[22] David W. Jeffery, Meagan D. Mercurio, Markus J. Herderich, Yoji Hayasaka, and Paul A. Smith. Rapid isolation of red wine polymeric polyphenols by solid-phase extraction. *Journal of Agricultural and Food Chemistry*, 56(8):2571–2580, 2008.

[23] Mahlo SM. The effectiveness of polyethylene glycol (PEG) and polyvinyl polypyrrolidone (PVPP) on removal of tannins from leaf extracts of selected medicinal plants in Limpopo Province. *African Journal of Biotechnology*, 11(43), 2012.